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<p>(21) International Application Number: PCT/GB96/02087</p> <p>(22) International Filing Date: 30 August 1996 (30.08.96)</p> <p>(30) Priority Data: 9517646.7 30 August 1995 (30.08.95) GB</p> <p>(71) Applicant (<i>for all designated States except US</i>): QUADRIZE LIMITED [GB/GB]; 2 Kings Yard, 19 High Street, Uxbridge, Middlesex UB1 1DG (GB).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (<i>for US only</i>): DODD, Peter, Jeremy [GB/GB]; "Lindean", Rickmansworth Lane, Chalfont St. Peter, Gerrards Cross, Buckinghamshire SL9 0LX (GB). STOCKWELL, Alan [GB/GB]; 7 Ravens Close, Knaphill, Woking, Surrey GU21 2LD (GB).</p> <p>(74) Agent: SILVERMAN, Warren; Haseltine Lake &amp; Co., Hazlitt House, 28 Southampton Buildings, Chancery Lane, London WC2A 1AT (GB).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report.</i></p>	

(54) Title: EMULSION FUELS AND THEIR USE IN GAS TURBINES

## (57) Abstract

Hydrocarbon oil-in-water emulsions, particularly those containing less than 1 ppm of sodium ions, provide a novel fuel for use in gas turbines. Relatively high efficiency combined with low cost represents significant benefits when utilising such emulsions as gas turbine fuel.

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## EMULSION FUELS AND THEIR USE IN GAS TURBINES

This invention relates to emulsion fuels and their use in gas turbines. More particularly, but not 5 exclusively, the invention relates to emulsion fuels based on viscous hydrocarbons derived from crude oil or on directly-produced high viscosity grades and the use thereof in gas turbines.

Fossil fuel power stations can be considered in 10 two categories: steam thermal power stations and gas turbine power stations. In the former, fuel is burnt to heat water in a boiler and produce steam which drives a turbine; the turbine then drives a generator which produces electricity. In some cases, the steam 15 is then condensed and returned to the boiler for reuse (a so-called "closed cycle"). The efficiency of the conversion of fuel to electricity in steam thermal power stations can be as low as about 30%.

In gas turbine power stations, a fuel, such as gas 20 or oil, is burnt in the combustor of a gas turbine so that the resulting combustion gases drive the turbine which drives a generator. The efficiency of this process is relatively low (about 30%) and so many gas 25 turbine power stations include a further step in which the hot combustion gases are used to heat water to steam, which is then used to drive a further generator. This further step may be in a closed cycle. The second step increases the efficiency of gas turbine power stations to as much as over 50%. Such a system is 30 known as a "combined cycle" system.

Refinery bottoms are the residual materials left after atmospheric distillation, vacuum distillation and other processes have been carried out in refineries as part of the conversion of crude oil to useful products. 35 Such refinery bottoms can be used by burning them in power stations. Unfortunately, these residual

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materials are difficult to handle because of their high viscosities and, if they are to be used as components of fuel oil, they are normally "cut-back" with more valuable products obtained in distillation of the crude  
5 oil. The quality of refinery bottoms depends to a large extent on the quality of the crude oil from which they are derived and the cost effectiveness of use of refinery bottoms as a fuel depends upon the proportion of more valuable components of crude oil distillation  
10 with which they have to be cut back, although there is little alternative to this use as the refinery bottoms must be disposed of.

In general, it is unavoidable that certain undesirable components of the crude oil are likely to  
15 be concentrated in the refinery bottoms. Such undesirable components include sulphur and heavy metals such as vanadium and nickel. These components can lead to the formation of undesirable combustion products such as sulphur oxides and vanadium oxides which can be  
20 found in the emissions from power stations. Generally, such emissions need to be cleaned before they can pass into the atmosphere. Such extra treatment can reduce the overall efficiency of converting the liquid fuel into energy.

25 Naturally, it would be highly desirable to be able to use refinery bottoms, effectively a waste product from the refinery processing of crude oil, to produce electricity with a high conversion factor.

Emulsion fuels containing large amounts of water  
30 are more readily handleable than refinery bottoms. In this connection, reference is made to GB-A-974,042 which relates to oil-in-water emulsion fuels comprising a petroleum oil of high viscosity, the oil comprising 60 vol. % of the emulsion such that the emulsion has a  
35 viscosity of less than 150 S.S.F. at 77°F (25°C). GB-A-974,042 proposes use of such oil-in-water emulsions in

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conventional steam thermal burners.

Also in the prior art, DE-A-2757419 proposes the use of water-in-oil emulsions having a water content of from 3 to 8 % in a gas turbine. Such emulsions consist 5 of droplets of liquid water in a continuous oil phase and, at least insofar as the use of refinery bottoms may be contemplated, water-in-oil emulsions manufactured from refinery bottoms as a base fuel will have significantly higher viscosities than oil-in-water 10 emulsions made from such a base fuel. In fact, there will be little significant difference between the viscosity of the water-in-oil emulsion and the viscosity of the base fuel itself.

In a first aspect of the invention, there is 15 provided a hydrocarbon oil-in-water emulsion for use as fuel in a gas turbine which is characterised by containing less than 1 ppm of sodium ions.

According to a second aspect of the present invention, there is provided a method of driving a gas 20 turbine which comprises combusting a hydrocarbon oil-in-water emulsion in the combustor of the turbine.

According to a third aspect of the present invention, there is provided the use of a hydrocarbon oil-in-water emulsion in driving a gas turbine by 25 combusting the oil-in-water emulsion in the combustor of the turbine.

The oil preferably comprises a refinery bottom material or a hydrocarbon oil having physical properties characteristic of a refinery bottom material 30 of oil-in-water emulsions as fuel for gas turbines, although it is to be appreciated that this aspect of the present invention is not limited to such oils. Indeed, lower density oils, such as diesel, can be used in the oil-in-water emulsion.

35 The oil-in-water emulsion may contain less than 1 ppm of sodium ions by using a water having less

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than 1 ppm of sodium ions as source water for the emulsion and/or washing the oil of excess sodium ions. In practice, the present invention may involve the use of deionised or any other water of low sodium ion content. In accordance with the invention, the term "oil-in-water emulsion" is to be understood as including within its scope oil-in-water/alcohol emulsions.

This invention is directed particularly to the use in oil-in-water emulsions of an oil phase having the following preferred properties. The oil preferably has a density at 15°C in the range of from 750 to 1050 kg/m<sup>3</sup>, more preferably in the range of from 980 to 1020 kg/m<sup>3</sup>. The kinematic viscosity of the oil at 25°C is preferably in the range of from 5 x 10<sup>3</sup> to 5 x 10<sup>6</sup> cSt, more preferably from 1 x 10<sup>4</sup> to 1 x 10<sup>6</sup> cSt. at 20°C. The oil moreover preferably has contents of sodium, vanadium and nickel in the ranges of from 0 to 500 (less than 100 in the first aspect of the invention), from 0 to 600, and from 0 to 150 ppm respectively, more preferably from 0 to 10, from 0 to 100 and from 0 to 20 ppm.

A wide range of viscous hydrocarbons have the above properties. Thus, it is possible to use light, medium, heavy and extra heavy crude oil, bitumen (both natural and manufactured), refinery residue oils of any description (e.g. fuel oil, atmospheric, vacuum, visbreaker, vacuum flashed visbreaker, precipitated asphalt), pitch and tar, particularly from tar ponds.

The hydrocarbons may contain asphaltene in an amount of from 0 to 100 w/w %, preferably from 0 to 20 w/w %; wax in an amount of from 0 to 30 w/w %, more preferably from 0 to 10 w/w % and sulphur in an amount of from 0 to 6, preferably from 0 to 4.5 w/w %.

As mentioned, the oil used for the oil-in-water emulsion may be produced as a result of the treatment

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of crude oil. A typical such treatment is as follows. The crude oil is transported to refinery for processing. After undergoing treatment, such as desalting, the crude oil is subjected to atmospheric distillation, that is, heated under atmospheric pressure until products are distilled from the crude. The valuable light products from this process include gasoline, kerosene and gas oil. The less valuable residual products from this process can either be used as the feed stock in oil-in-water emulsion production or for supply to a vacuum distillation column. In the latter case, the residual products are subjected to further heating, but this time under a vacuum. Again, lighter products are produced as well as viscous residual products. Again, it is the latter which may either be used as a feedstock for oil-in-water emulsion production or directed to further processing via a visbreaker and possibly to asphalt producing equipment. Whatever the chosen process, residual waste material will always be produced at each stage and it is this material which can be utilised in the production of the required emulsion fuel.

The waste material can be stored at any suitable temperature. However, it must be cooled/heated to about 100°C for mixing with water to form the oil-in-water emulsion.

Typical feedstocks for oil-in-water emulsion fuel are residues produced from Arabian crude oils (light, medium or heavy). The vacuum residue of Arabian Light crude typically has the following chemical and physical properties:

C-85.0 % by weight; H-10.7 % by weight; N-0.34 % by weight; S-3.9 % by weight; ash-0.01 % by weight; vanadium 63 ppm; nickel 17 ppm; iron 1 ppm; sodium < 1 ppm; gravity ° API of

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6-10; viscosity of 350 cSt at 100°C.

Alternative feedstocks are natural bitumens such as those produced in Alberta or in the Orinoco belt of Venezuela. Analysis details of natural bitumens from 5 Venezuela are presented in US-A-4,801,304.

In a typical method for forming the oil-in-water emulsion, the still fluid hydrocarbon waste residue or directly-produced hydrocarbon is pumped to a point where it is mixed with water and a material which 10 reduces the interfacial tension between the oil and the water, for example a surfactant and/or a polymer, using static mixers, in-line mechanical mixers or a combination of both.

The oil-in-water emulsion produced will typically 15 have an oil/water ratio (w/w) in the range of from 65:35 to 90:10, preferably from 70:30 to 85:15. An oil droplet size range of up to 200 µm, preferably up to 100 µm, is to be contemplated. The droplet size may vary within wide parameters but it is preferred that 20 the emulsion contains oil droplets greater than 150 µm diameter to an extent of less than 3 % w/w, more preferably less than 2 % w/w. The emulsion itself will preferably have a density of from 825 to 1050, more from 980 to 1020 kg/m<sup>3</sup> at 15°C and a 25 viscosity at 25°C and less than 100 sec<sup>-1</sup> of less than 2000 cSt, more preferably less than 1000 cSt. By operating in accordance with the invention, it is possible to produce a liquid fuel having a gross calorific value of from 28-32 MJkg<sup>-1</sup>, more preferably 30 29-31 MJkg<sup>-1</sup> and a net calorific value of 26-30 MJkg<sup>-1</sup>, preferably 27-29 MJkg<sup>-1</sup>.

A most preferred oil-in-water emulsion to be employed in the practice of the present invention is characterised by a water content of about 30 % by 35 weight, a mean droplet size in the range from 10 to 70 µm and possibly a combustion-improving additive, which

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is preferably water soluble, more preferably a Mg salt such as magnesium nitrate or magnesium sulphate, the combustion additive having alkali metal content of up to 100 ppm.

5 When a surfactant is utilised in producing the emulsion, it may be selected from anionic surfactants, non-ionic surfactants and cationic surfactants, or mixtures thereof. A surfactant is added in amount in the range of from 0.1 to 5.0 % by weight of the  
10 hydrocarbon residue, preferably from 0.1 to 1.0 % by weight of the hydrocarbon residue. Suitable non-ionic surfactants for use in the process include ethoxylated alkylphenols, ethoxylated alcohols, ethoxylated sorbitan esters and mixtures thereof. Cationic  
15 surfactants which may be used include hydrochlorides of fatty diamines, imidazolines, ethoxylated amines, amido-amines, quaternary ammonium compounds and mixtures thereof. Anionic surfactants which may be used include esterified long-chain carboxylic acids,  
20 sulphuric acid ester and esterified sulphonic acids and mixtures thereof. Preferred anionic surfactants are represented by alkyl aryl sulphonates and alkyl aryl sulphates and mixtures thereof.

Various specific methods are available for the  
25 manufacture of oil-in-water emulsions. One specific method is described in WO85/03646 in which mixing is effected under low shear conditions in the range 10 to 1000 reciprocal seconds in such manner that an emulsion is formed comprising highly distorted oil droplets  
30 having mean droplet diameters in the range 2 to 50  $\mu\text{m}$  separated by thin interfacial films. Another method is disclosed in GB-A-2262054 which describes the production of bimodal oil-in-water emulsions containing both relatively large oil droplet sizes in the range of  
35 10 to 40  $\mu\text{m}$  and small droplet sizes in the range of less than or equal to 5  $\mu\text{m}$ . A further method of

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forming an emulsion is known from GB-A-974,042 mentioned earlier herein.

The oil-in-water emulsion which is produced can be used immediately or can be stored prior to 5 transportation by pipeline, barge or ocean-going vessel to be stored again at the site of a combustion facility at which it is to be combusted in a gas turbine.

In accordance with a certain embodiments of the present invention, the emulsion is fed to the 10 combustion chamber of a gas turbine where it is converted into energy.

Two types of gas turbine can be used; gas turbines operated in open cycle, in which the exhaust gases are released directly into the atmosphere, or gas turbines 15 operated in combined cycle, in which the exhaust gases are passed through a heat recovery steam generator to extract additional heat before discharge to the atmosphere. The thermal efficiency of oil-in-water emulsions burnt in a gas turbine operated in open cycle 20 is in general similar to that of a conventional steam thermal power station, i.e. between about 30 and 40 %, depending on the design and operating conditions of the facility. However, the preferred mode of burning oil-in-water emulsions is in a gas turbine in combined 25 cycle, where thermal efficiencies of between about 40 and 50+% can be achieved.

Combustion of the emulsion fuel proceeds with a turbulent diffusion flame at temperatures and pressures which depend on the design of the turbine. The 30 presence of water in the fuel reduces the peak flame temperature and oxygen requirements in the early stages of combustion. As a consequence, the formation of both thermal- and fuel-derived NOx is reduced to levels lower than would be achieved with an equivalent heavy 35 fuel oil or water-in-oil emulsion.

In order to reduce vanadium pentoxide formation,

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which leads to corrosion of the turbine blades, water-soluble or more expensive oil-soluble magnesium compounds are conventionally injected separately into fuel just upstream of the combustion chamber. These 5 magnesium compounds serve two purposes; firstly, as viscosity modifier for the fuel, if indeed they are needed as such, and secondly as important corrosion inhibitors necessary to protect the turbine blades. However, oil-in-water emulsions have the advantage that 10 the cheaper water-soluble magnesium compounds can be added when the emulsion is formed. Therefore, the use of an oil-in-water emulsion with an added integral inhibitor obviates the need for additional equipment used to add the inhibitor at the combustion stage..

15 Because of the high sulphur content of refinery bottoms, sulphur dioxide and sulphur trioxide will be formed during combustion of oil-in-water emulsions formed from such refinery bottoms and will be present in the exhaust gases. Therefore, the exhaust gases can 20 be treated using an appropriate Flue Gas Desulphurisation (FGD) process. This process takes place immediately downstream of the combined cycle plant.

By way of summary, reference is now made to the 25 accompanying drawing which is a flow diagram showing the various stages in the production and use of an oil-in-water emulsion.

In the first stage, crude oil is produced at an oil field. It is then processed at a refinery or at 30 the oil field to produce a residue for use in forming an emulsion. Alternatively, the emulsion can be formed from a material extracted directly, e.g. a heavy, extra-heavy or natural bitumen, in which case the refinery stage can be omitted. Next, the oil-in-water 35 emulsion is produced; this can take place at the refinery or at a power station or, in the case of

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directly-produced materials, at the oil field. The resulting oil-in-water emulsion is then burnt in a gas turbine to produce energy. The exhaust gases are then used to raise steam in a waste heat boiler for the 5 second electricity generation stage of the combined cycle. Finally, the combustion gases are cleaned in a Flue Gas Desulphurisation unit prior to release to the atmosphere.

By working in accordance with the present 10 invention, the benefit is obtained of working with oil-in-water emulsions in a field where the use of such emulsions has not previously been contemplated.

Thus, when high viscosity refinery bottoms are used as the base fuel for the oil-in-water emulsion, 15 benefit is obtained from the easy handling properties of such emulsions in that they have significantly lower viscosities than either the base fuel or water-in-oil emulsions manufactured from the base fuel. Oil-in-water emulsions also induce lower line pressures. 20 upstream of the combustor. Because oil-in-water emulsions have lower viscosity, lines upstream of the combustor do not need to be heated to the same extent as with the base fuel or with water-in-oil emulsions.

More particularly, in preferred embodiments, use 25 is made of cheaper, lower quality, denser and more viscous oils than have hitherto found practical and economic application in gas turbine combustion. The likely upper viscosity limit at the combustor for oil-in-water emulsions would be about 15 cSt.

30 Insofar as the combustion properties are concerned, because of the pre-atomised nature of the fuel which exists when combustion is being carried out in a gas turbine, very good carbon burn out can be achieved. As mentioned, the presence of water in the 35 fuel means that the peak flame temperature is lowered and there is a consequent reduction of NO<sub>x</sub> and

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particulates produced. Moreover, turbine blades need to be cleaned less frequently with oil-in-water emulsions than with water-in-oil emulsions or with heavy or viscous fuels without any water in them.

- 5 Insofar as combustion additives are concerned, it is possible to use water-soluble combustion additives which are considerably cheaper than combustion additives which are oil-soluble.

Use of an oil-in-water emulsion containing less  
10 than 1 ppm of Na<sup>+</sup> has been found to be desirable for the purpose of minimising corrosion of the turbine blades.

In summary, use is made in accordance with the present invention of a low-cost energy source whose practical and economic use in gas turbine operation has  
15 not hitherto been contemplated. When in a combined gas turbine steam or other secondary cycle configuration, gas turbines achieve greater efficiency in converting the fuel to energy compared to a conventional steam thermal power station and, with the enhanced cost-  
20 production due to use of a low cost hydrocarbon source, operation is particularly economical. The use of such a low cost hydrocarbon source means that, in some applications, it can be economical to use emulsion fuels in open cycle gas turbine operation.

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CLAIMS:

1. An hydrocarbon oil-in-water emulsion for use as fuel in a gas turbine which is characterised by containing less than 1 ppm of sodium ions.
- 5 2. An emulsion as claimed in claim 1 which is an oil-in-deionised water emulsion.
3. An emulsion as claimed in claim 1 or 2, wherein the oil has a density at 15°C in the range of from 750-1050 kg/m<sup>3</sup>, preferably 980-1020 kg/m<sup>3</sup>.
- 10 4. An emulsion as claimed in any preceding claim, wherein the oil has a kinematic viscosity of from 5 x 10<sup>3</sup> to 5 x 10<sup>6</sup> cSt, preferably from 1 x 10<sup>4</sup> to 1 x 10<sup>6</sup> cSt. at 20°C.
5. An emulsion as claimed in any preceding claim, 15 wherein the oil has contents of vanadium and nickel in the ranges of from 0 - 600 and 0 - 150 ppm respectively, preferably from 0 - 100 and 0 - 20 ppm respectively.
6. An emulsion as claimed in any preceding claim, 20 wherein the oil is light, medium, heavy or extra heavy crude oil, bitumen, refinery residue oils selected from fuel oil, atmospheric, vacuum, visbreaker, vacuum flashed visbreaker and precipitated asphalt, pitch and tar.
- 25 7. An emulsion as claimed in any preceding claim, wherein the oil is a vacuum residue of Arabian Light, Medium or Heavy crude oil.
8. An emulsion as claimed in any preceding claim, which has an oil/water ratio (w/w) in the range of from 30 65:35 to 90:10, preferably from 70:30 to 85:15.
9. An emulsion as claimed in any preceding claim, wherein the oil droplet size is up to 200 µm, preferably up to 100 µm.
10. An emulsion as claimed in any preceding claim, 35 wherein oil droplets greater than 150 µm diameter are present to an extent of less than 3% w/w, more

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preferably less than 2% w/w.

11. An emulsion as claimed in any preceding claim which has a density of from 825 to 1050, preferably 980 to 1020 kg/m<sup>3</sup> at 15°C.

5 12. An emulsion as claimed in any preceding claim, which has a viscosity at 25°C at less than 100 sec<sup>-1</sup> of less than 2000 cSt, preferably less than 1000 cSt.

13. An emulsion as claimed in any preceding claim which has a gross calorific value of from 28-32 MJkg<sup>-1</sup>,

10 preferably 29-31 MJkg<sup>-1</sup> and a net calorific value of from 26-30 MJkg<sup>-1</sup>, preferably 27-29 MJkg<sup>-1</sup>.

14. An emulsion as claimed in any preceding claim which contains a surfactant in any amount of from 0.1 to 5.0 % by weight of the hydrocarbon oil.

15 15. An emulsion as claimed in any preceding claim which additionally contains a water soluble or oil soluble magnesium compound.

16. A method of driving a gas turbine which comprises combusting a hydrocarbon oil-in-water emulsion in the 20 combustor of the turbine.

17. A method as claimed in claim 16, wherein the water of said emulsion contains less than 1 ppm of sodium ions.

18. A method as claimed in claim 16, wherein the 25 emulsion contains a water soluble or oil soluble magnesium salt, the emulsion having an alkali metal content of up to 500 ppm.

19. A method as claimed in claim 16, which comprises combusting a hydrocarbon oil-in-water emulsion as 30 claimed in any one of claims 1 to 15.

20. The use of a hydrocarbon oil-in-water emulsion in driving a gas turbine by combusting the hydrocarbon oil-in-water emulsion in the combustor of the turbine.

21. The use of claim 20 wherein the emulsion is an 35 emulsion as claimed in any one of claims 1 to 15.

22. The use of claim 20 or 21 which is in a gas

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turbine operated in open cycle.

23. The use of claim 20 or 21, in which the gas turbine is operated in combined cycle, with hot gases from the combustor of the turbine being utilised to  
5 drive a steam turbine.

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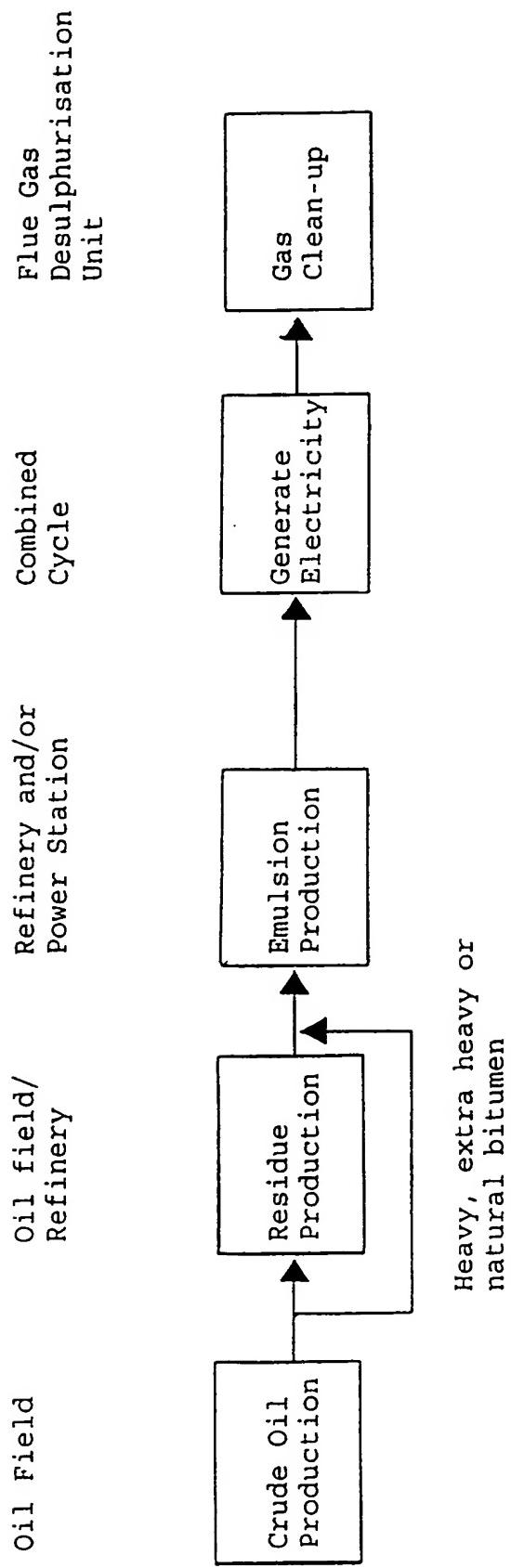
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Figure 1.



## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 96/02087

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C10L1/32

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 682 101 (AUER GERHARD) 15 November 1995	1,2
P,A	*ABSTRACT* see claims 1,2 ---	16,17, 19-21
A	GB,A,2 191 783 (INTEVEP SA) 23 December 1987 -----	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

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## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 96/02087

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0682101	15-11-95	WO-A-	9525154	21-09-95
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